

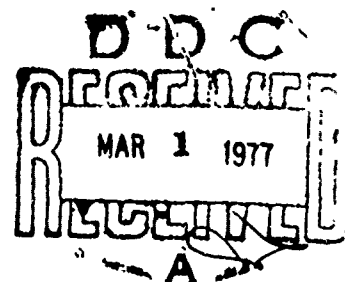
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THE EFFECTS OF UV LIGHT
ON TNT AND OTHER EXPLOSIVES
IN AQUEOUS SOLUTION

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Explosives in Aqueous Solution

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THE EFFECTS OF UV LIGHT ON TNT AND OTHER
EXPLOSIVES IN AQUEOUS SOLUTIONS

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J. L. OSMON

ABSTRACT

The role of each of four bench-scale UV systems in the treatment of aqueous explosive solutions is discussed. Studies relating the effects of acetone and H_2O_2 in the treatment are reviewed. Under given conditions, UV light (254 nm) in conjunction with small concentrations of H_2O_2 results in the elimination of such explosives as TNT (^{alpha} trinitrotoluene), RDX (cyclonite), HMX (homocyclonite), 2,4 DNT (dinitrotoluene), 2,6 DNT and Explosive D (ammonium picrate) from their aqueous solutions. Analyses have shown that explosive disappearance is accompanied by a decrease in TOC after one hour of exposure. No significant concentrations of any related conversion products were detected in the one hour photolysates. Studies incorporating 1,3,5 labeled ¹⁴C-TNT have indicated that the TNT molecule is cleaved and converted to ¹⁴CO₂ upon such treatment. UV treatment of bomb-loading effluents containing 221 ppm TNT and 148 ppm RDX successfully resulted in the elimination of these explosives and their conversion products.

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THE EFFECTS OF UV LIGHT ON TNT AND OTHER EXPLOSIVES IN AQUEOUS SOLUTIONS

INTRODUCTION

Water discharges and effluents from ammunition production plants, loading facilities and demilitarization operations are contaminated with explosive compounds from these processes. They are very difficult to degrade biologically and chemical treatment generally results in minor modifications of the compounds without their actual decomposition. Ultraviolet light, under given conditions, can effect the destruction of many types of explosive compounds in aqueous solutions. Through our studies we have discovered that UV light in combination with hydrogen peroxide is an effective, efficient method for treating water contaminated with such explosives as TNT (trinitrotoluene), RDX (cyclonite), HMX (homocyclonite), 2,4 DNT (dinitrotoluene), 2,6 DNT and Explosive D (ammonium picrate). The process has also been successful in treating pink water effluents (TNT contaminated water becomes pink upon exposure to sunlight) which also contain RDX.

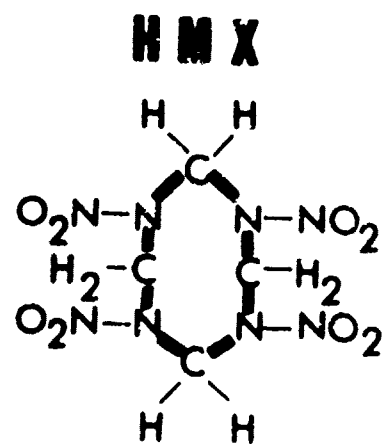
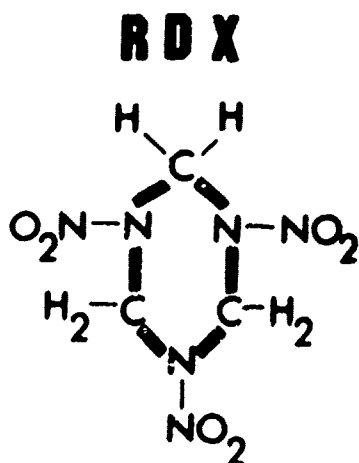
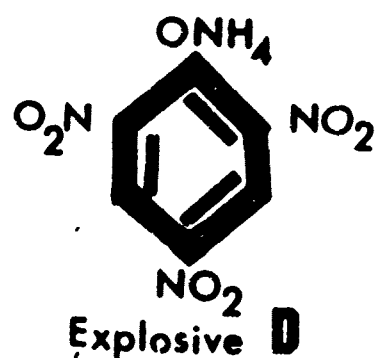
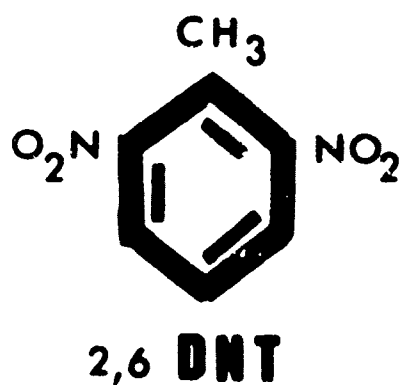
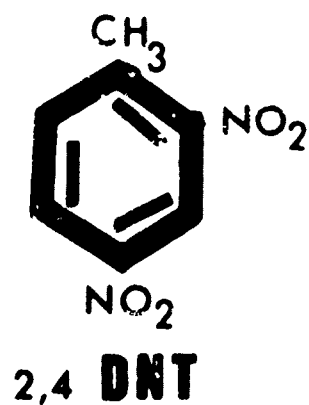
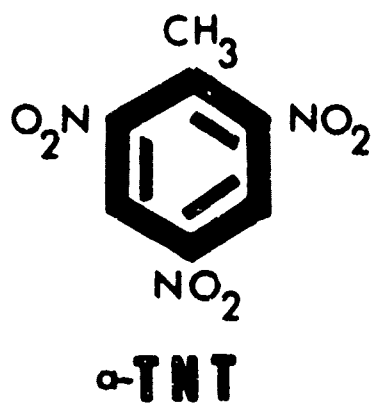
Structures of all the compounds are found in Figure 1.

EXPERIMENTAL

Bench-Scale Models

The effect of UV light on aqueous solutions of explosives has been studied in several bench-scale models. A germicidal UV lamp (GE, 30 watt, #G30T8, 240-260 nm primary wavelength band) was incorporated as the source of UV energy in each of the test models which included open irradiation, mini-, continuous flow and static or batch systems.

FIG.1. Chemical Structures



UV-Open Irradiation System

Saturated aqueous solutions of TNT (100 ppm), prepared from a 50,000 ppm TNT acetone concentrate (1 ml/500 cc distilled H₂O), were irradiated in open containers over a period of 24 hours (1). The distance of the solutions from the UV source was controlled. The solutions and their photolysates were analyzed by gas chromatography (GC)¹ and thin-layer chromatography (TLC)² to determine TNT concentration and the types of TNT-related polynitroaromatic conversion products which were present before and after irradiation. (These GC and TLC procedures were used consistently in all our studies and unless otherwise noted, they will not be specifically referenced in the remainder of the paper.)

For a more complete description of experimental parameters see reference (1).

UV Mini-System

Aqueous solutions of 1,3,5 ¹⁴C-TNT were irradiated in a mini-system consisting of a Vycor tube (as the reaction vessel) connected to a charcoal trap for the trapping of volatile organics and an alkali trap for collection of ¹⁴CO₂ (2). The design of the system is illustrated in Figure 2. A sample volume of 2 ml was irradiated during each treatment. The conditions of the procedure were varied with respect to time, availability of atmospheric gases and the type of trapping systems employed.

The radioactivity of the solution, its photolysate, CO₂ and charcoal was monitored by a Liquid Scintillation Spectrometer using Multisol (Isolabs, Inc.) as the scintillation cocktail. Analysis for TNT and its related polynitroaromatic conversion products was performed by gas chromatography and thin-layer chromatography.

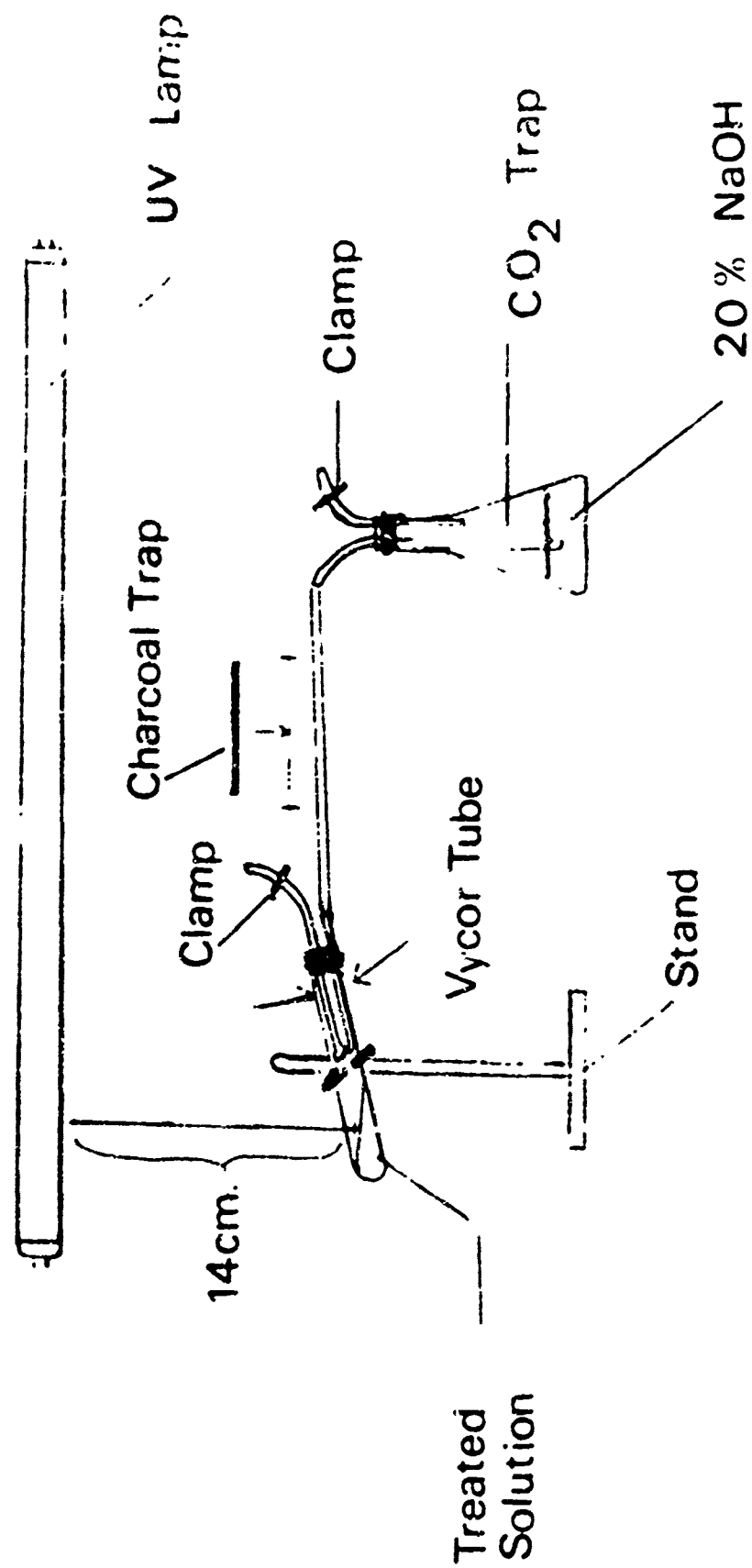


FIG. 2. UV mini-system

For specific details concerning operating parameters and analytical procedures consult reference (2).

Aqueous solutions of 2,4 and 2,6 DNT were treated in the UV mini-system, which was modified to exclude the alkali and charcoal traps for the labeled samples. A 100 ppm solution of each was prepared from 50,000 ppm concentrates of the compounds in acetone. A 7.5 ml sample of each was irradiated in the Vycor tube, which was completely filled. Each tube was irradiated at a distance of 14 cm from the UV source for a period of two weeks. Analyses of the DNT solutions and their photolysates were performed by gas chromatography and thin-layer chromatography.

An identical study was performed with an aqueous solution of RDX (50 ppm) prepared from an acetone concentrate of 50,000 ppm (0.5 ml/500 cc distilled water). The samples were analyzed by liquid chromatography³ (LC) to detect RDX or related products.

A solution of pink water was also treated in the mini-system. It was analyzed by GC and TLC to determine the concentration of TNT and to detect any polynitroaromatics which were present before treatment. A quartz tube (rather than a Vycor one) was used as the reaction vessel for the pink water in the UV mini-system treatment. A 2.5 ml volume of solution was exposed for 138 hours at a distance of 14 cm from the UV source. One ml of the photolysate was sampled for TLC analysis and the remaining portion was sampled for GC determination.

UV Continuous Flow System

A bench-scale test system was developed to treat larger volumes of explosive solutions per unit time. The new model, a continuous flow system, allowed the direct contact of the solution with the UV lamp as it was continuously recirculated from a reservoir for repeated exposure. See Figure 3.

A pyrex jacket surrounding the UV lamp contains the solution for irradiation. The depth of the liquid in the jacket is 0.3 cm. The jacket, itself, ($d = 3$ cm, $l = 78.7$ cm) retains approximately 200 ml of solution when completely full. The lamp is suspended in the jacket by O-rings on either end.

A total volume of 500 ml is circulated from a reservoir flask via a peristaltic pump past the UV source about 3 times each hour. The reservoir flask is equipped with a stopper in which are inserted two pieces of glass tubing serving as influent and effluent ports for the flask. The effluent port is connected to a peristaltic pump by means of latex tubing (o.d. = 8 mm, i.d. = 4 mm). The sample is thus pumped from the reservoir through the jacket and reenters the flask through tubing connecting the effluent port of the jacket with the reservoir's influent port. The flow-rate is approximately 27 ml per minute.

The solution in the reservoir is maintained at 27°C by a water bath regulated with a thermoregulator. A thermometer fixed in the stopper of the reservoir flask is used to monitor the temperature of the liquid. The solution in the flask is constantly stirred by a magnetic stirrer.

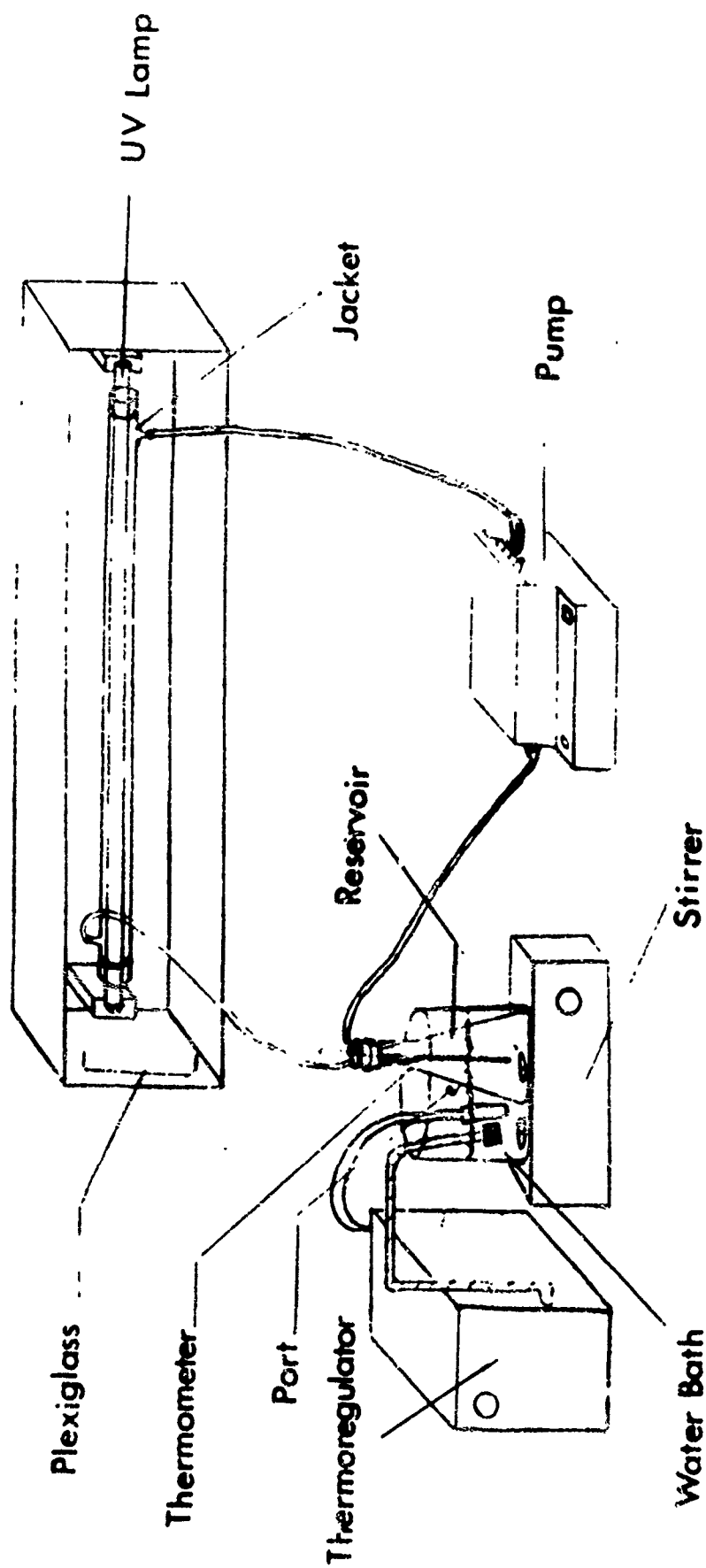


FIG. 3. UV continuous-flow system (c.f.s.)

Samples for analyses are removed directly from the solution in the reservoir. The final sample is representative of the pooled solutions of the jacket and flask.

Saturated water solutions of TNT, RDX, HMX, 2,6 DNT and 2,4 DNT were prepared from concentrates in acetone for irradiation in the continuous flow device. The preparation of the aqueous solutions of explosive involved the addition of a small volume of the concentrates (10,000 ppm or 50,000 ppm of the explosive) to the distilled water. The solutions were mixed so as to induce the volatilization of the acetone from the solution before irradiation. Samples of the freshly prepared solutions of the explosives were analyzed by GC and/or LC and TLC^{2,4} to determine concentration of the explosive and the presence of any conversion products.

Table 1 illustrates the concentration and mode of preparation of each of the explosive aqueous solutions treated in the system. These concentrations are generally representative of the saturation limits of the explosive in water.

At the initiation of each treatment in the UV continuous flow system, the jacket was filled with the respective aqueous solution and a 0-time sample was taken for the necessary analyses. The water bath was cooled to maintain the temperature of the reservoir liquid at 27°C. This measure limited the effects of temperature on the photochemical process. At the termination of the experiment the solution from the jacket and tubing was pooled with the reservoir sample for the respective analyses.

TABLE 1. Preparation of aqueous explosive solutions
from acetone concentrates of the explosives

EXPLOSIVE	DESIRED* CONCENTRATION	VOL. CONCENTRATE (ml)/500 ml DISTILLED WATER
TNT	100	1.0 ml of 50,000 ppm TNT
RDX	50	0.5 ml of 50,000 ppm RDX
HMX	5	0.25 ml of 10,000 ppm HMX
2,6 DNT	100	1.0 ml of 50,000 ppm 2,6 DNT
2,4 DNT	100	1.0 ml of 50,000 ppm 2,4 DNT

*ppm

The photolysates were analyzed for cyanide⁵, nitrate⁶, nitrite⁷, and ammonia⁸. These compounds were thought to represent some of the nitrogenous end-products of the photolysis of the compounds involved.

Gas samples were taken during the irradiation of a TNT aqueous solution. These were analyzed by GC⁹ to detect the presence of carbon dioxide, carbon monoxide, methane and nitrogen oxides. The pH of the solutions was monitored.

UV Continuous Flow Method - Acetone Concentration Varied

It was inadvertently discovered that the presence of acetone was required for the UV continuous flow method to be effective in treating solutions containing TNT and its polynitroaromatic conversion products. To determine the relationship between acetone concentration and its effectiveness in the UV continuous flow treatment of TNT solutions, the acetone concentration introduced into the TNT solution before treatment was controlled.

Acetone-free saturated solutions (100 ppm) of TNT were prepared by dissolving 50 mg of TNT in 500 ml of distilled water. The following acetone concentrations were tested in the system: 0.01, 0.02, 0.10, 0.20, 0.25, 0.50 and 1.0%. The acetone was added directly before exposure. Each of these acetone-TNT solutions was treated in the continuous flow device for a period of 21.5 hours. Samples for GC and TLC analyses were taken at 0, 10, 15 and 30 minutes and at 1, 1.5, 2, 2.5, 3, 3.5, 4, 5 and 21.5 hours of exposure. The solutions and their 21.5 hour photolysates were analyzed also for the presence of cyanide⁵, nitrate⁶, nitrite⁷, and ammonia⁸.

UV Continuous Flow Treatment of Bomb-Loading Effluent

Samples of effluent containing TNT and RDX (pink water) were analyzed by GC and TLC before treatment in the UV system. The solutions were then treated in the continuous flow device. Acetone was not specifically added to these effluents.

Samples for GC and TLC analysis in one study were taken at 0, 0.5, 1, 1.5, 3, 5, 8, 24, 25, 27, 32, 48 and at 49 hours of irradiation at which point the assay was terminated. In another study, with effluent from the same source, another 500 ml portion was treated in the system with samples taken at 0, 0.5, 2, 3, 5, and 69 hours for the respective analyses.

Color changes and pH variations of the solutions were monitored at each sampling interval in both studies.

UV Continuous Flow - H₂O₂ Treatment of TNT Solutions

Because of acetone's characteristic volatility and because it contributes to the TOC of the solution to be treated, hydrogen peroxide, which has greater oxidative potential, was tested in the UV continuous flow system for its effectiveness in treating TNT solutions. As in the case of acetone, the hydrogen peroxide concentrations were controlled to determine the optimum effective concentration to be used in the UV continuous flow system. Solutions of TNT (100 ppm) were prepared by dissolving 50 mg TNT/500 ml distilled water. TNT solutions containing 0.01, 0.02, 0.05, 0.10, 0.5, 1.0, 1.5 and 2.0% H₂O₂ were treated. Each of these H₂O₂-TNT solutions was treated in the system over a 24-hour period with samples taken at 0, 10, 15 min. and 1, 2, 3, 4, 5, and

24 hours of exposure for GC and TLC analyses. The photolysates and their original solutions were analyzed for Total Organic Carbon (TOC) concentration (Beckman 915 TOC Analyzer).

Additional analyses included GC¹⁰, GC-mass spectrometry¹¹ and TLC (7).

UV Static System - H₂O₂ Treatment of TNT Solutions

To determine the effects of constant exposure of aqueous TNT solutions to UV light, the continuous flow system was modified. The jacket and UV lamp of the continuous flow system were the basic components of the static system. The pump was used to fill the jacket with the solution but was disconnected from the static system during its operation. The inlet tubing of the jacket was closed with a screw clamp to prevent leakage of the solution from the system. The outlet port remained open to allow any gases produced to escape. If gases produced in the system were to be measured and trapped, a water displacement apparatus was attached to the outlet by means of tubing. The gases were then analyzed by GC⁹ and IR (infrared) spectrophotometry¹³.

Since peroxide was found to be a successful oxidizing agent in treating TNT in the continuous flow studies, the peroxide concentrations used in the static system were varied to incorporate the concentrations which effected the best results in the earlier UV continuous flow studies. These concentrations included 0.02, 0.05, 0.07, 0.1, 0.2 and 0.3% H₂O₂.

The standard GC and TLC analyses for TNT and the polynitro-aromatics were performed on all 0-time and irradiated samples. The

periods of irradiation generally ranged from 0 to 5 hours. The pH and TOC load of the solutions and their photolysates was also monitored. Peroxide concentrations were determined semi-quantitatively by means of peroxide quants (EM Quant, Ether Peroxide Test, E. Merck). The temperature of the treated solution was measured.

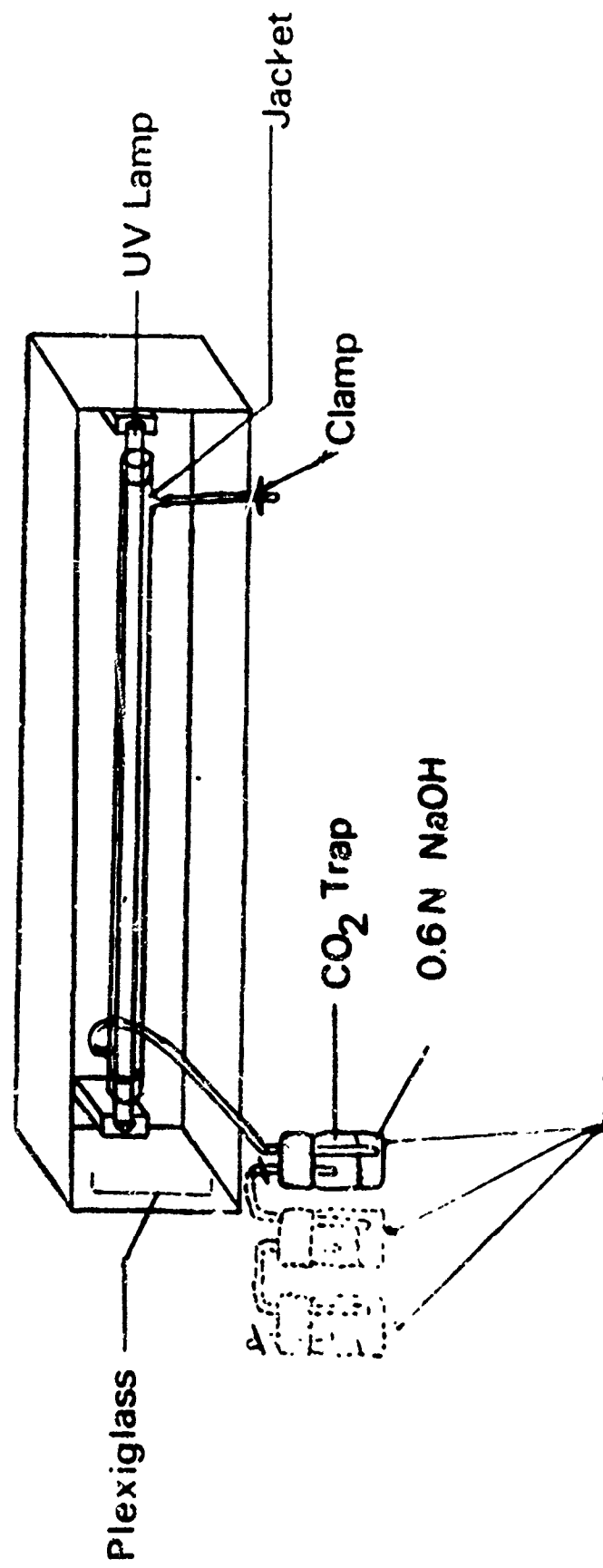
UV-H₂O₂ Static System Treatment of ¹⁴C-TNT

An aqueous solution of ¹⁴C-TNT (1,3,5 label) with a specific activity of 1100 dpm/mg was prepared by dissolving 30 mg ¹⁴C-TNT in 300 ml of distilled water to yield a 100 ppm solution. To this was added a quantity of peroxide to yield a 0.1% concentration. Samples were taken before and after peroxide addition for determination of activity. Measurements were made on a liquid scintillation spectrometer using Multisol (Isolabs, Inc.) as the scintillation cocktail.

The jacket of the system was filled with a volume of 180 ml of the aqueous ¹⁴C-TNT solution. An alkali trap consisting of a scintillation vial filled with 4.5 ml 0.6N NaOH (with 0.01% TRITON X for trapping enhancement) was attached by means of a short piece of rubber tubing to the effluent port of the jacket for collection of ¹⁴CO₂ (See Figure 4). This trapping system is a modification of the method used by Klaus and Meezun (3).

At the termination of the irradiation process at 5 hours, a slight vacuum was pulled to allow the gases in the tubing to be passed through the alkali trap. The 4.5 ml of the 0.6N NaOH was then divided into three aliquots, 1.5 ml each, and distributed into each of three vials for determination of ¹⁴CO₂ activity. Multisol (15 ml) was again

FIG. 4. UV Static system with CO₂ traps (s.s.)



used as the scintillation cocktail in each vial. Due to the chemiluminescence caused by the presence of the alkali the activity of each was allowed to stabilize overnight.

The activity of the 5 hour photolysate was determined and the necessary GC, TLC, and TOC analyses were performed on it and on the 0-time solutions (with and without peroxide).

The previous radioassay was repeated with the following exceptions: three alkali traps were used instead of the one; and the system was purged with N_2 at the termination of the assay for 12 minutes at a flow rate of 15 ml/min. These alterations were made to increase the efficiency of the trapping system and to determine if the $^{14}CO_2$ was escaping trapping.

UV- H_2O_2 Static Treatment: Explosive D, HMX, RDX, 2,4 DNT, 2,6 DNT

Aqueous solutions of the following compounds were prepared by dissolving the respective compound in distilled water to yield the indicated concentration: Explosive D (500 ppm), HMX (5 ppm), RDX (50 ppm), 2,6 DNT (100 ppm) and 2,4 DNT (100 ppm). Hydrogen peroxide was added to each of the solutions to yield a concentration of 0.1% (which seemed to be the most effective concentration employed in the UV-static treatment of TNT). All solutions were treated in the static system from 0 to 5 hours. Samples were taken before treatment and at various intervals and analyzed by GC, LC and TLC^{2,4}. Peroxide concentration was monitored semi-quantitatively as indicated in a previous assay. TOC determinations were also made on all samples.

Explosive D concentration was determined colorimetrically. Such determinations were made with and without peroxide. All solutions

were adjusted to pH 2 to prevent shifts in coloration caused by the acidic nature of the solution and the presence of picric acid. The absorbances of various concentrations of Explosive D solutions with and without peroxide were measured and standard curves prepared for the determination of unknown concentrations.

RESULTS AND DISCUSSION

Initial Studies: Open and Mini-Irradiation Systems

In our preliminary studies using UV light we irradiated saturated solutions of TNT (100 ppm) in open containers at a fixed distance from a UV germicidal lamp (primary wavelength 240-260 nm). TNT concentration decreased with increased time of exposure. After 24 hours only 170 ppb TNT remained in the photolysate (our detectability limits in this case with gas chromatography or thin-layer chromatography was 10 ppb). A number of photolytic conversion products were detected in the 24-hour photolysate by GC and TLC. The irradiated material itself was rusty-red in color, comparable to "pink water". (Aqueous solutions of TNT become pink after exposure to sunlight due to the existence of photolytic conversion products.)

For a more complete description of results see reference (1).

To eliminate the effects of evaporation and concentration in irradiating TNT solutions in open systems, a mini-system was developed in which small volumes of explosive solutions could be irradiated in a closed environment. The system also was designed for radiotracer studies incorporating ^{14}C -TNT. A charcoal trap for volatile organics and an alkali trap for $^{14}\text{CO}_2$ were included in the system to give some indication

as to what is happening to the TNT molecule upon irradiation. Using ^{14}C -TNT labeled in the 1, 3, 5 positions we discovered that UV light induced the cleavage of the TNT ring structure with the resulting formation of $^{14}\text{CO}_2$. In one study, after 312 hours of irradiation of a 100 ppm solution of ^{14}C -TNT 17% of the activity was found as $^{14}\text{CO}_2$, 55% was trapped on the charcoal (volatile organics captured), and 5% remained in the photolysate which was found to be void of TNT or related polynitroaromatics. About 23% of the activity remained unrecovered. Some of this activity is speculated to have been in the form of methane since this gas was found to be present in significant amounts in the atmosphere above the photolysate.

Other aqueous explosive solutions were successfully treated in the mini-system. These include RDX, HMX, 2,4 dinitrotoluene and 2,6 dinitrotoluene and solutions of pink water containing TNT and RDX. None of these explosives were found to be present in the photolysates after 312 hours of exposure. Furthermore, no conversion products were detected.

For additional information concerning results and discussion of this system see reference (2).

UV Continuous Flow System: A Successful Procedure

The UV mini-system discussed earlier was impractical and inefficient. Only small volumes could be treated per unit time. Exposure periods were long. It did, however, provide enough significant data to serve as a prototype for the development of a larger, more efficient system - the UV continuous flow system. All the explosive solutions treated in the continuous flow device were treated successfully. Aqueous solutions of TNT, RDX, HMX, 2,4 DNT, 2,6 DNT and bomb-loading effluents

containing mixtures of TNT and RDX were irradiated and the explosives apparently decomposed by the treatment.

UV Continuous Flow Treatment for TNT

In Study I all detectable TNT was exhausted from the original (100 ppm) TNT solution between three and five hours of irradiation in the continuous flow system. No polynitroaromatic conversion products were detected in the 5 hour photolysate or thereafter. Carbon dioxide and methane were found to be present in significant concentrations in the system. Since the TNT solution was made from a TNT concentrate in acetone, the CO₂ and CH₄ are probable products of the photolysis of acetone and TNT (explained later in the paper). Nitrogen oxides were not detected.

Table 2 illustrates the results of the continuous flow treatment of a TNT solution (Study I). It emphasizes the relationship of TNT concentration and interval of exposure and the chemical and physical characteristics of the untreated and treated solution between 0 and 29 hours of irradiation.

As seen from Table 2 the pH drops from 6.0 to 3.3. The color and turbidity of the solution varies until the solution is clarified and decolorized by 22.5 hours of irradiation. The polynitroaromatics as determined by TLC are no longer detectable by 3 hours of irradiation, but there are as many as five detected in the 1 hour photolysate and a fluorescent product persists between 5 and 22.5 hours of irradiation.

These results are similar to the results of another study (Study II) performed on a saturated TNT solution in the UV continuous flow system. See Table 3.

TABLE 2. STUDY I: The properties of a saturated aqueous TNT solution and its photoiysates after treatment in the continuous flow system. (29 hours). This study was extended for 72 hours but there were no major changes between 29 and 72 hours.

<u>SAMPLE #</u>	<u>UV EXPOSURE (HRS.)</u>	<u>pH</u>	<u>COLOR/CLARITY OF THE SOLUTION</u>	<u>GC RESULTS TNT (ppm)</u>	<u>TLC RESULTS TNT/# of Con-version Products</u>
1	0	6.0	Colorless/clear	90	TNT/0
2	1.0	-	Rusty/turbid	1	TNT/5
3	3.0	-	Amber/slight turbidity	0	*Trace TNT/3
4	5.0	-	Yellow/clear	0	0/1 ^F
5	6.5	-	Straw/clear	0	0/1 ^F
6	10.0	-	Straw/clear	0	0/1 ^F
7	22.5	-	Colorless/clear	0	0/1 ^F
8	25.0	-	Colorless/clear	0	0/0
9	27.0	-	Colorless/clear	0	0/0
10	29.0	3.3	Colorless/clear	0	0/0

*Detectability of TNT with TLC system ~10 ppb in this case but the detectability of TNT with GC system ~50 ppb.

F = Fluorescent product (375 nm)

TABLE 3. STUDY II: The properties of a saturated aqueous TNT solution and its photolysates after treatment in the continuous flow system (24 hours).

<u>SAMPLE #</u>	<u>UV EXPOSURE (HRS.)</u>	<u>pH</u>	<u>COLOR/CLARITY OF THE SOLUTION</u>	<u>GC RESULTS TNT (ppm)</u>	<u>TLC RESULTS TNT/# of Conversion Products</u>
1	0	6.0	Colorless/clear	109.5	TNT
2	2	3.2	Rusty/turbid	0	Trace TNT/3
3	4	3.1	Amber/clear	0	0
4	6	3.2	Straw/clear	0	0
5	24	3.3	Colorless/clear	0	0

TABLE 4. Specific ion concentrations and the percent nitrogen recovered as such in the 24 hour and 72 hour TNT photolysates.

<u>ION</u>	<u>ION CONCENTRATION (ppm)</u>		<u>%TOTAL N RECOVERED**</u>	
	<u>24 hr.</u>	<u>72 hr.</u>	<u>24 hr.</u>	<u>72 hr.</u>
Cyanide	0.064	0.01*	0.17	-
Nitrate	0.020*	1.00	-	0.03
Nitrite	0.020*	0.001*	-	-
Ammonia	6.10	10.09	27.69	49.54

* Insignificant concentrations as compared with 0 hour controls.

**We are assuming in this case that all the nitrogen was derived from the original concentration of TNT, as determined by GC analyses.

Available nitrogen = 20.26 ppm in Study I and 16.7 ppm in Study II.

As in the earlier study the acidity increases upon exposure. The solution eventually becomes colorless and clear after going through a color variation. TNT can no longer be detected after four hours of exposure and the polynitroaromatic products disappear by 4 hours. However, unlike the result of the first study the second study illustrated that all detectable products were eliminated by four hours of exposure. The first study indicated that one detected product, very unlike all polynitroaromatics previously isolated, fluoresced at 375 nm, and remained in the photolysate through 22.5 hours of exposure. After this time it was eliminated. This small discrepancy may possibly reflect a variation in the original acetone concentration in the solution, since the acetone concentration was not intentionally controlled in these studies.

Table 4 illustrates the results of the analyses for cyanide, nitrate, nitrite and ammonia in the 72 hour TNT photolysate of Study I and the 24 hour TNT photolysate of Study II.

Ammonia was present in very significant concentrations in both photolysates, although the 72 hour photolysate contained more than 1.5 times the concentration of the 24 hour photolysate. From the results it seemed that the generation of ammonia was related to the time of exposure. It is possible that a variation of the concentration of acetone in each system may have effected such results. Additional information, however, presented later in the paper does not appear to support this. Repeated studies controlling such variables as exposure time and acetone concentration may help resolve the question.

Only a trace concentration of cyanide was detected in the 24 hour photolysate. The pH was too low for a significant concentration to

have been dissolved in the solution. Even if significant concentrations were produced, the cyanide would have escaped as a gas under these conditions.

The existence of only a small concentration of nitrate, if any, found in the photolysates may probably be best explained by the reactivity of the ionic species formed from the irradiation of the acetone with the nitrate, resulting in the formation of ammonia. An explanation to this effect is found later in this paper.

The failure to detect nitrite ions in the photolysates can probably be explained by this theory as well as their instability in solution under these conditions.

UV Continuous Flow Treatment: The Acetone Question

In our studies involving the UV continuous flow treatment of aqueous TNT solutions, it was inadvertently found that acetone was necessary for the complete elimination of the polynitroaromatic conversion products normally associated with the photochemistry of TNT in solution. Saturated aqueous solutions of TNT were not totally treatable in the UV systems if acetone was not present. TNT could be eliminated by UV treatment, but the polynitroaromatic products formed from the irradiation of TNT were not destroyed in the absence of acetone. In its absence, the TNT solutions were never decolorized.

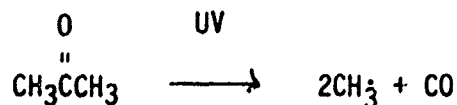
It was not specifically determined if acetone was necessary for the decomposition of RDX, HMX, 2,6 DNT and 2,4 DNT in the UV continuous flow system. As was noted in the first section, these explosive solutions were prepared from acetone concentrates. It is therefore a possibility

that acetone could have played a major factor in the UV treatment of these solutions as well.

Photochemistry of Acetone in Aqueous Solution

A previous discussion concerning the photolysis of acetone and its possible effects on existing species such as nitrate requires some clarification. The mechanism involved in the photochemical decomposition of acetone is based on methyl radical formation. These radicals seek hydrogen to return to a stable state or even may possibly contribute hydrogen to other existing species. Some of the basic products of the reaction, would be the production of methane, carbon monoxide and CO₂.

The following demonstrates the proposed reaction of the acetone in aqueous solution under the influence of UV energy (254 nm):



(Carbon monoxide is very unstable and is oxidized very easily to become CO₂). Carrying this reaction further the following is postulated to occur in the presence of an organic compound (R) such as TNT:



The organic compound is now in an unstable state and is very vulnerable to further decomposition. In the case of TNT or another polynitroaromatic the ring structure is probably very vulnerable to photochemical oxidation and to subsequent ring cleavage.

It is theorized that the ionic species such as nitrate can be reduced in this system by contributing oxygen for the oxidation of the carbon monoxide, a product of acetone photolysis. The acetone may also

contribute the hydrogen for the ultimate reduction of the nitrate species to ammonia.

As mentioned previously, CH_4 and CO_2 have been found to be present in significant quantities during the UV continuous flow treatment of aqueous TNT solutions. Since these solutions were prepared from acetone concentrates, it is not unreasonable to assume that a significant amount of the methane and CO_2 were produced from the acetone alone. However, it is also feasible, although not provable from this data, that some of the CO_2 and CH_4 could have been the products of the photolysis of TNT itself. Earlier studies, using the UV mini-system, in which 1, 3, 5 ^{14}C -TNT solutions were irradiated, have shown that $^{14}\text{CO}_2$ was produced and that this product could have only resulted from the actual cleavage of the ring structure. Other supporting evidence includes the fact that TNT and all its associated polynitroaromatic conversion products were apparently eliminated after four hours of exposure in the system and that no other ring structures were detectable from analyses by TLC or GC-mass spectroscopy.

UV Continuous Flow Treatment: RDX, HMX, 2,4 DNT, 2,6 DNT

The continuous flow treatment was apparently successful in the ultimate elimination of RDX, HMX, 2,4 DNT and 2,6 DNT as well as TNT from their aqueous solutions. As mentioned previously, acetone concentrates of these explosives were used in preparation of their aqueous solutions. It must be emphasized that the absolute need for acetone in this treatment remains to be proven.

Table 5 summarizes the results of the study involving the treatment of aqueous solutions of RDX and HMX. Both RDX and HMX were eliminated by 2 hours of irradiation as determined by LC and TLC analyses. Only RDX and HMX were detected by TLC at 0-time. Unfortunately, the first interval at which a sample was taken was 2 hours in each system so it cannot be determined exactly how quickly the reaction occurred and exactly how vulnerable each of these compounds was to the UV treatment.

Both 2,6 DNT and 2,4 DNT were also eliminated by the UV continuous flow treatment. Results of this study are found in Table 6.

It is interesting to speculate that the fluorescent product which appears after the irradiation of the 2,4 DNT may be the same product which appears upon the irradiation of 2,4,6 TNT and that the nitrated number 4 position common to both molecules may be a key to the identity of this product. After two hours of irradiation of a 2,6 DNT solution, the 2,6 DNT and all related conversion products were eliminated. The fluorescent product was not detected in any of the 2,6 DNT photolysates.

Analyses of the 2,6 DNT and 2,4 DNT photolysates for cyanide, nitrate, nitrite and ammonia yielded the results found in Table 7. Note that the 2,6 DNT photolysate was the result of 72 hours of irradiation and the 2,4 DNT photolysate was the result of 78 hours of irradiation. The 2,4 DNT solution was irradiated longer in hopes of destroying the fluorescent irradiation product with prolonged exposure. The intensity of the product as determined by TLC, appeared to decrease between 72 and 78 hours of exposure.

TABLE 5. The properties of aqueous solutions of HMX and RDX before and after UV irradiation in the continuous flow system as determined by LC and TLC.

<u>EXPOSURE (HOURS)</u>	<u>LC RDX (ppm)</u>	<u>pH</u>	<u>TLC DETECTABLE PRODUCTS</u>	<u>LC HMX (ppm)</u>	<u>pH</u>	<u>TLC DETECTABLE PRODUCTS</u>
0	45.5	5.8	RDX	5.6	6.9	HMX
2	0	3.8	0	0	3.6	0
4	0	3.6	0	0	3.2	0
6	0	3.5	0	0	3.1	0
24	0	3.4	0	0	3.0	0

TABLE 6. The properties of aqueous solutions of 2,6 DNT and 2,4 DNT before and after treatment in the UV continuous flow device as determined by LC and TLC.

<u>EXPOSURE (HOURS)</u>	<u>LC 2,6 DNT (ppm)</u>	<u>pH</u>	<u>TLC DETECTABLE PRODUCTS</u>	<u>LC 2,4 DNT (ppm)</u>	<u>pH</u>	<u>TLC DETECTABLE PRODUCTS</u>
0	91	6.3	2,6 DNT	65.3	6.7	2,4 DNT
2	1.7	3.5	0	0.4	3.9	1 ^F
4	0	3.7	0	0.2	3.6	1 ^F
6	0	3.7	0	0	3.5	1 ^F
8	0	3.8	0	0	3.5	1 ^F

F = fluoresces at 375 nm.

TABLE 7. Specific ion concentrations and the percent nitrogen recovered as such in the 72 hour 2,6 DNT photolysate and 78 hour 2,4 DNT photolysate.

ION	ION CONCENTRATION (ppm)		%TOTAL N RECOVERED**	
	2,6 DNT	2,4 DNT	2,6 DNT	2,4 DNT
Cyanide	0.029	0.01*	0.11	-
Nitrate	2.11	0.5	3.33	0.79
Nitrite	0.18*	0.01*	-	-
Ammonia	6.81	0.61	40.17	4.98

* Insignificant concentration as compared with 0 hour controls.

**We are assuming that all nitrogen was derived from the original concentrations of DNT as determined by LC analysis. Available nitrogen = 13.9 ppm in the 2,6 DNT solution and 10.05 ppm in 2,4 DNT solution.

Ammonia, as in the case of TNT, appeared to be the predominant species in both the 2,6 DNT and 2,4 DNT photolysates. However, the 2,6 DNT contained a little more than eight times as much ammonia. It appeared as if the nitrate group in the number 6 position may have contributed significantly to the production of ammonia in the system. Obviously, more work is necessary to prove or disprove this speculation. The acetone concentration, once again, may play a factor in this reaction. Due to its volatility, it is almost impossible to control its concentration and this may partially be responsible for the level of its reactivity with the nitrate groups upon irradiation.

In general, the UV continuous flow treatment of aqueous solutions of TNT, RDX, HMX, 2,4 DNT and 2,6 DNT proved relatively successful. Each of these compounds were eliminated in a matter of a few hours, as were any detectable polynitroaromatic conversion products normally associated with the irradiation of TNT or DNT solutions. The presence of acetone was found to be necessary for the successful elimination of the polynitroaromatic conversion products formed from the UV irradiation of TNT solutions. The exact influence of acetone on the UV treatment of other explosive solutions remains to be determined.

Although the amount of acetone introduced into solution was somewhat controlled by the amount of explosive concentrate added to yield the desired concentration, there was no precaution taken to control the amount of time elapsed between its introduction into solution and the irradiation of the solution. Obviously, acetone being volatile, was lost with time. Originally, we had not considered the presence of the acetone to be relevant for the reaction. It was only later, when we

prepared TNT solutions by directly dissolving the crystals in distilled water and irradiated these solutions without the subsequent elimination of the polynitroaromatic products and without decolorization of the solutions, that we discovered its necessity.

The preparation of the aqueous explosive solutions from their respective crystals is an overnight process, since the compounds are not very soluble in water. It is less time consuming to introduce the compounds into solution from acetone concentrates. These solutions could then be treated almost immediately after the addition. Consequently, we followed this preparation procedure as much as possible, since it saved time and the solutions were freshly prepared before treatment (at least within a matter of a few hours). The discovery concerning the necessity of the acetone for the treatment of TNT and its conversion products caused a change in this procedure.

UV Continuous Flow Treatment of TNT Solutions with Varied Acetone Concentrations

To help determine the optimal efficiency of the UV continuous flow treatment of TNT solutions in the presence of acetone, the acetone concentration was varied. Each aliquot of acetone was introduced into the system immediately before irradiation to restrict its volatilization as much as possible. The information found in Table 8 summarizes the results of this study.

The data in Table 8 illustrates that a general trend concerning the relationship between acetone and TNT concentrations emerged from the study after 0.5 hours of exposure. An average of 70% of the TNT was

TABLE 8. Illustration of TNT concentration at each exposure interval with each concentration of acetone.

ASSAY	%ACETONE	EXPOSURE (HRS.)			
		0.5	2.5	~5	21.5
		TNT (ppm)			
1	0.01	25.8	0.14	0.02	0
2	0.02	38.0	0.16	0.20	0
3	0.05	25.9	0.09	0.42	0
4	0.10	15.1	0.50	0	0
5	0.20	15.0	0.15	0	0
6	0.25	7.5	0.02	0	0
7	0.50	7.8	0.03	0	0
8	1.00	6.6	0.10	0	0

The average concentration of all 0-time samples = 107.6 ppm TNT

eliminated by this time when 0.01, 0.02 or 0.05% acetone was initially present. About 85% of the TNT disappeared when 0.1 or 0.2% acetone was used and an average of 93% of the TNT was eliminated by 30 minutes when 0.25, 0.50 or 1.00% acetone was initially introduced into the solution. By 2.5 hours of treatment over 99.5% of the TNT had disappeared in each case. The apparent slight increase in TNT concentration between 2.5 and 5 hours in Assays 2 and 3 and the fluctuations in all cases at 2.5 hours could be attributed to experimental error and the efficiency of extraction of the aqueous TNT solution for GC analysis. Aqueous solutions containing small concentrations of TNT are more likely to be affected by experimental error.

The TLC work had indicated that by 2.5 hours of irradiation using concentrations of 0.25 to 1.0% acetone all detectable polynitroaromatic by-products were eliminated. Between 5 and 21.5 hours of irradiation with all concentrations of acetone all polynitroaromatics were apparently successfully treated. However, a fluorescent product was detected in all 21.5 hour photolysates initially containing from 0.2 to 1.0% acetone. The higher the acetone concentration the greater the intensity of the product. This was detected by examining the developed TLC plates under 375 nm UV light. The product, possibly the same as that found in studies discussed earlier, was not found in 21.5 hour photolysates which initially contained 0.01 to 0.1% acetone. This product was also not detected in any irradiated samples which were treated in the presence of 0.01 to 0.05% acetone. The concentration or existence of this fluorescent compound appears to be directly related to the initial concentration of acetone employed in the TNT solution.

Table 9 illustrates the results of the analyses of all the acetone treated 21.5 hour photolysates for cyanide, nitrate and ammonia. No significant concentrations of nitrite were found in any of these irradiated solutions.

The concentration of ammonia, once again as in other studies, dominated the other detected ionic species. The significant cyanide concentration of the 1.0% acetone photolysate cannot go unnoticed. This high value remains questionable until further studies can support it. In general, there was a significant drop in the nitrate concentration in photolysates with increasing acetone concentration from 0.05 to 1.0%. The same seemed to be true for the ammonia concentration. The lower levels of acetone, 0.01 and 0.02%, seemed to yield results inconsistent with the general trend. Whether this is the norm or an anomaly has yet to be determined.

The concentration of ammonia present in the 21.5 hour 0.2% acetone-UV treated TNT solution relates very well with the value obtained in an earlier study of a 24 hour TNT photolysate with the same initial acetone concentration (a 1 ml acetone TNT concentrate per 500 ml water would yield a 0.2% acetone concentration). The initial study illustrated that 6.1 ppm ammonia was found in the 24 hour photolysate. The current study indicated that 5.6 ppm ammonia was detected in the 21.5 hour photolysate. All factors considered, the value appears to be repeatable under given conditions if we consider the small time difference insignificant.

The results of the UV-acetone studies indicated that the 1% concentration of acetone was the most effective of all the concentrations

TABLE 9. Specific ion concentrations of 21.5 hour irradiated TNT solutions originally prepared with varying acetone concentrations.

<u>%ACETONE</u>	<u>-CN</u>	ppm <u>-NO₃</u>	<u>-NH₃</u>	%TOTAL N RECOVERED AS**		
				<u>-CN</u>	<u>-NO₃</u>	<u>-NH₃</u>
				(Available N = 20 ppm)		
0.01	0.35	3.4	4.4	0.95	3.74	18.04
0.02	0.10	4.2	5.6	0.27	4.62	22.96
0.05	0.10	3.4	7.0	0.27	3.74	28.70
0.10	0.03	1.8	7.0	0.08	1.98	28.70
0.2	0.04	1.8	6.6	0.11	1.98	27.06
0.5	0.12	1.0	4.6	0.32	1.10	18.86
1.0	3.5	1.2	4.4	9.45	1.32	18.04

All the above values were corrected by values obtained for untreated controls.

**We are assuming that all the nitrogen was derived from the original TNT concentration as determined by GC analyses. The average value of TNT of all the untreated samples was used in this case (107.6 ppm).

employed in eliminating TNT as quickly as possible (93.4% reduction of TNT by 30 minutes). There were no polynitroaromatics detected after 2.5 hours of irradiation with 0.25, 0.5 or 1.00% acetone-UV treatment. However, an unidentified fluorescent product was evident in each of these 21.5 hr. photolysates. The intensity of this product appeared to be directly proportional to the acetone concentration. The fact that it was so persistent indicates the necessity of its identification. This is necessary because this product may be present in concentrations which are detrimental toxicologically and which may pose a greater threat to the environment than TNT and/or its polynitroaromatics. The application of 0.20% acetone or less in the treatment effected the elimination of the TNT as well as the fluorescent product between 5 and 21.5 hours of irradiation. Obviously, more samples should be taken between 5 and 21.5 hours of irradiation with concentrations at and below 0.2% acetone to determine when and if the product is completely eliminated by such treatment.

Loading Effluents Treated Successfully in UV Continuous Flow System

Pink water samples were obtained from the vicinity of a bomb loading operation at NAVWPNSUPPCEN Crane. Whatman-filtered effluents were found to contain average concentrations of 221 ppm TNT and 148 ppm RDX. TNT and RDX adsorbed to fine residual sediment in the samples obviously contributed to such high values. Acetone was not added for the treatment. The conditions were not optimized and yet TNT slowly disappeared with time as did the number and types of polynitroaromatic conversion products. By 49 hours of exposure all TNT and all detectable

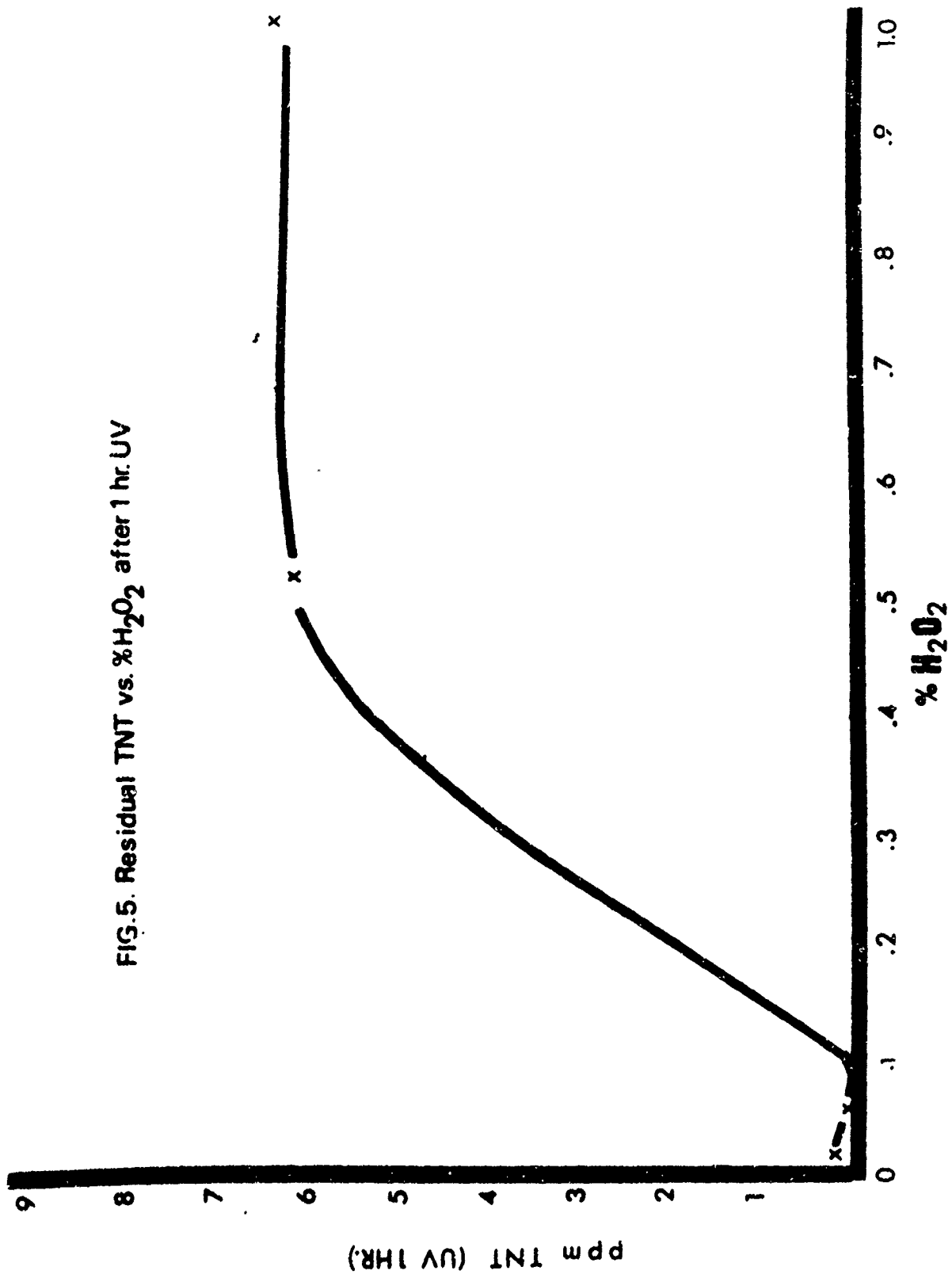
polynitroaromatics, with the exception of a trace of one product (barely discernible by TLC) were eliminated in the continuous flow system. RDX had disappeared between 0.5 and 3 hours of irradiation. Repeated studies substantiated these findings. These results produced under less than optimum conditions added credence to the feasibility of using such a system in the treatment of military waste effluents on a larger scale.

The Value of the UV-H₂O₂ Treatment

Because of its volatility and its contribution to the organic carbon load, acetone was not considered to be a good agent to use in enhancing the photolytic treatment of explosive waste solutions. An agent which would be a good oxidizer in the photochemical system, which would produce more reactive ionic species, and which would not increase the organic carbon load of the solution was more desirable. Consequently, hydrogen peroxide was chosen and tested in the UV continuous flow system to determine its effect on the treatment procedure.

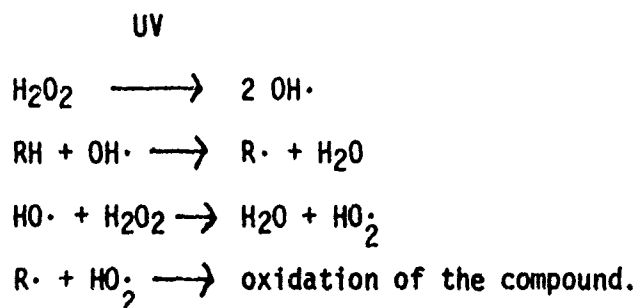
Saturated aqueous solutions of TNT (100 ppm) containing concentrations of H₂O₂ ranging from 0.01% to 2.0% were treated in the UV continuous flow system with varying degrees of success. From such studies it appeared that the residual concentration of TNT in an irradiated solution was not directly proportional to the concentration of peroxide originally employed. Figure 5 illustrates this relationship. Note that there is a narrow range of H₂O₂ concentrations (0.02 to 0.05%) which appear to be very effective in eliminating TNT by one hour of irradiation. On either side of this range the effectiveness of the UV-peroxide treatment of TNT is diminished. If the curve is extended to include the residual

FIG. 5. Residual TNT vs. %H₂O₂ after 1 hr. UV



concentration of TNT in solutions originally containing 1.5 and 2.0% H_2O_2 , the curve assumes a sigmoidal shape since 7 and 9 ppm TNT, respectively, were found in these photolysates.

It is theorized that the presence of excessively large concentrations of H_2O_2 in the system upset the stoichiometric balance between it and the material with which it reacts to force it to react with itself. Thus, a good portion of it is wasted in this manner. To understand this better, the following equations help illustrate the mechanism of the action of UV light on the peroxide and the subsequent reaction of its photo-degradative species with organic material (R):



*If R is representative of an aromatic species such as TNT, it is apparently cleaved upon subsequent oxidations.

As seen from the equations, the UV light initiates the breakdown of peroxide to hydroxyl radicals which seek hydrogen to stabilize themselves. The organic molecule may react with these radicals leaving it in an unstable state. This could result in its eventual destruction by subsequent oxidation reactions. This is postulated to happen to TNT and its polynitroaromatics upon exposure to UV light in the presence of peroxide.

One of the prominent reaction products of the H_2O_2 -UV treatment of TNT solutions was found to be trinitrobenzene, indicating that the methyl group was excised from the ring early during the treatment making the structure more vulnerable to attack and subsequent ring cleavage.

Effect of H₂O₂ Concentration on TNT in the UV-Continuous Flow System

The employment of higher concentrations of peroxide in treating TNT solutions, although not very efficiently, does result in the eventual elimination of TNT and an eventual reduction in the TOC of the solution. For instance, 1.5% H₂O₂ in the UV treatment induces the elimination of TNT by 6 hours as compared with its elimination between 1 and 2 hours using 0.1% H₂O₂. The TOC is reduced to about 6 ppm in 2 hours with 0.1% H₂O₂ whereas it is reduced to this level in 6 hours using 1.5%. See Figure 6. Obviously a large amount of peroxide is being wasted in one case. This is indicative that greater efficiency can be achieved using a concentration of peroxide more stoichiometrically compatible with the concentration of TNT available.

Table 10 summarizes the results of the relationship between the residual TNT concentration in an irradiated solution versus the concentration of peroxide introduced initially.

Results of analyses of three photolysates, representing initial H₂O₂ concentrations of 2, 1 and 0.5%, for cyanide, nitrate, nitrite and ammonia are found in Table 11. Note that the solutions have been irradiated for 48, 24 and 27 hours respectively.

These results were unlike the results of the assays employing acetone. Instead of ammonia being the dominant species, nitrate concentrations were high in each photolysate. Assuming that all the nitrate was derived from that available from the TNT, over a fifth of the available nitrogen can be accounted for as nitrate in each case. Another interesting discovery was that the ammonia concentration was over 30 times greater in the 1% H₂O₂ photolysate than in the 0.5% H₂O₂ photolysate, although there was only a three hour difference in exposure between the two.

FIG. 6. Exposure vs. TOC (c.f.s.) with 1.5 & 0.1% H_2O_2

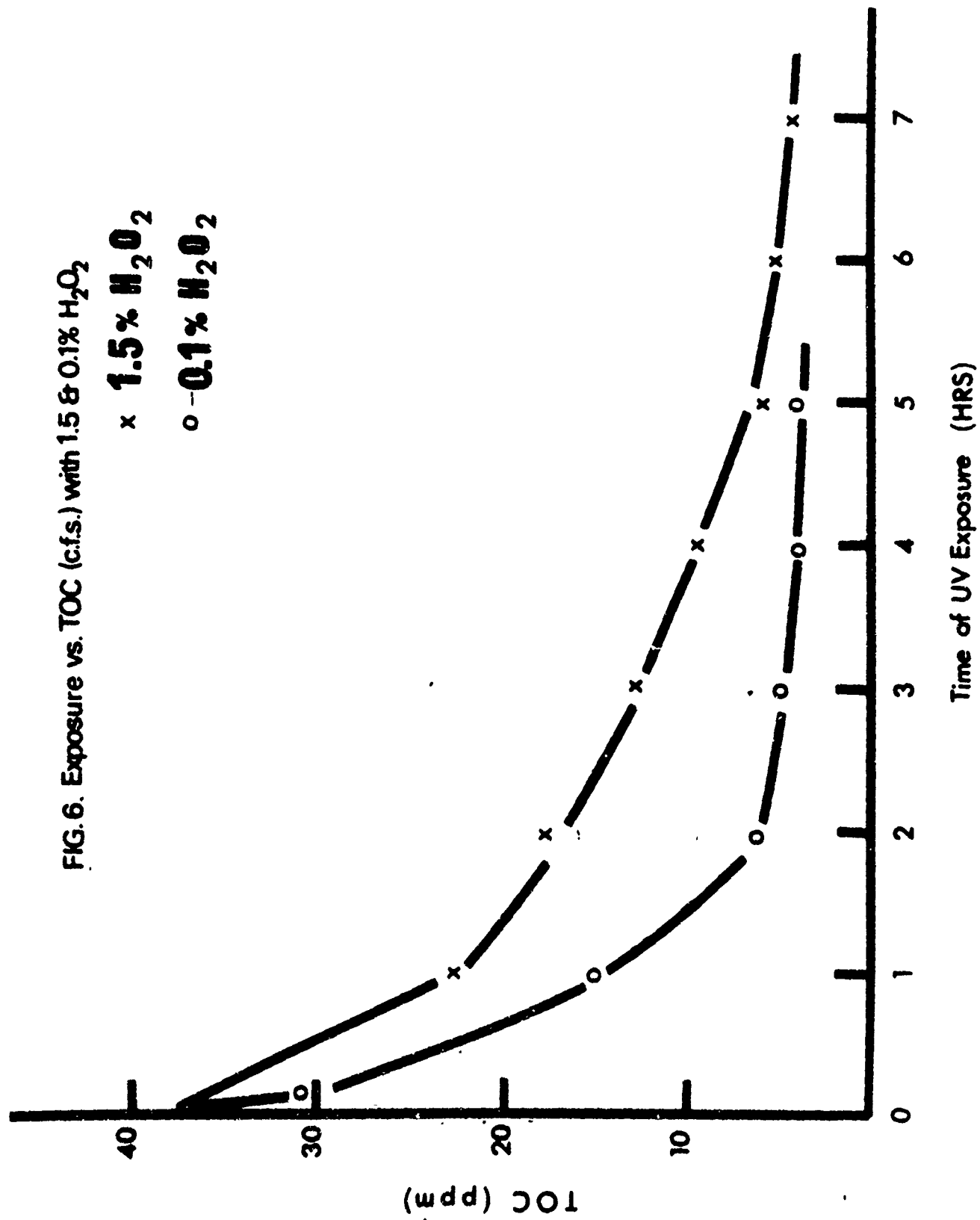


TABLE 10. Effect of peroxide concentration on TNT elimination with time of exposure in the continuous flow system.

<u>%H₂O₂</u>	<u>EXPOSURE TIME</u>						
	<u>10 min.</u>	<u>15 min.</u>	<u>1 hr.</u>	<u>2 hr.</u>	<u>3 hr.</u>	<u>4 hr.</u>	<u>5 hr.</u>
	<u>TNT (ppm)</u>						
2.0	52.9	-	10.2	8.0	5.4	3.5	-
1.5	-	56.6	7.3	2.1	0.6	0.5	0.4
1.0	-	35.5	6.2	3.5	0.8	0.1	0
0.5	60.4	-	6.4	1.8	-	0	0
0.05	35.1	-	0	0	0	-	0
0.02	-	33.0	0.18	0	-	0	0
0.01	-	28.0	0.30	0.1*	-	0	0

*Sample taken at 2.5 hour instead of 2 hr.

The average concentration of all unirradiated TNT solutions as determined from GC analysis = 95 ppm

TABLE 11. Specific ion concentrations of TNT photolysates originally containing 2, 1 and 0.5% H₂O₂ and the %N recovered in each case.

<u>ION</u>	<u>2% H₂O₂ (48 hr.)</u>		<u>1% H₂O₂ (24 hr.)</u>		<u>0.5% H₂O₂ (27 hr.)</u>	
	<u>ppm</u>	<u>%N**</u>	<u>ppm</u>	<u>%N</u>	<u>ppm</u>	<u>%N</u>
Cyanide	0.05	0.15	0.26	0.80	2.20	6.79
Nitrate	18.00	22.00	16.60	20.24	18.00	20.81
Nitrite	0.18	0.14	0.07*	-	0.10*	-
Ammonia	2.90	13.26	2.00	9.04	0.13	0.28

All values were corrected by untreated control values.

* These values were comparable to control values.

**We are assuming all nitrogen was derived from the available TNT.

Nitrogen available = 17.6 ppm.

We have also determined that the concentration of nitric acid necessary to yield a pH of 3.3 as detected in the 24 hour TNT-H₂O₂ photolysates, is approximately equivalent to the average concentration of nitrate that has been detected in this study.

As mentioned previously, trinitrobenzene had been found to be an important intermediate product in the UV-H₂O₂ treatment of TNT solutions in the continuous flow system. An overview of the study seems to illustrate that independent of the concentration of peroxide employed originally, the greatest concentration of trinitrobenzene was always found in photolysates between 1 and 2 hours of irradiation. Analysis by liquid chromatography verified these results, which were originally demonstrated by thin-layer chromatography.

TLC analyses of all 24 hour photolysates, dependent on the original peroxide concentration, have indicated that between 10 and 100 ppb of trinitrobenzene were still evident. The higher the original concentration of peroxide, the greater the residual trinitrobenzene concentration.

Batch Treatment of TNT Solutions in the UV-H₂O₂ Static System

UV irradiation of batches of saturated aqueous TNT solutions (~100 ppm) in the presence of low concentrations of peroxide yielded the "best" results of all the studies. Constant UV irradiation of a batch of TNT solution in the presence of 0.02 to 0.2% H₂O₂ was shown to be more effective than related studies in the continuous flow device. At all these peroxide levels TNT was eliminated between 0 and 1 hr. of

irradiation (samples were not taken before 1 hour since complete decolorization was usually achieved between 30 min. and 1 hour). Traces of trinitrobenzene (>10 <50 ppb) were found in all 5 hour photolysates except the 0.1% H₂O₂ irradiated solution. Figure 7 illustrates the relationship between the TOC load and the original H₂O₂ concentrations employed after 5 hours of treatment. The best results were achieved using a 0.1% H₂O₂ concentration in which only 2 to 3 ppm TOC was detected. The TOC load was reduced by 76% using 0.02% H₂O₂ and by over 90% using 0.1%. The TOC load of the 0.1% H₂O₂ TNT solutions was decreased by this percentage after only 2 hours of irradiation. There was no major reduction in TOC between 2 and 5 hours with this concentration of H₂O₂ (see Figure 8), although trinitrobenzene was no longer detectable at 5 hours as it was at all previous intervals. However, as previously mentioned, trinitrobenzene was detected only in the parts per billion range (>10 <50 ppb) and would not have contributed significantly to a reduction in TOC upon its disappearance.

The monitoring of the peroxide concentration in all cases have shown that it was generally exhausted between 1 and 2 hours of irradiation, independent of the original concentration.

The temperature of the irradiated solutions after 5 hours of exposure was found to be between 48 and 49°C.

Static UV-H₂O₂ Treatment of ¹⁴C-TNT

Studies with 1, 3, 5 labeled ¹⁴C-TNT confirm that the TNT ring structure was indeed vulnerable to the UV-peroxide treatment in the static system. A 0.1% H₂O₂ concentration, apparently the most effective

FIG. 7. TOC vs. % H_2O_2 after 5 hrs. UV (s.s.)

UV - 5 HRS.

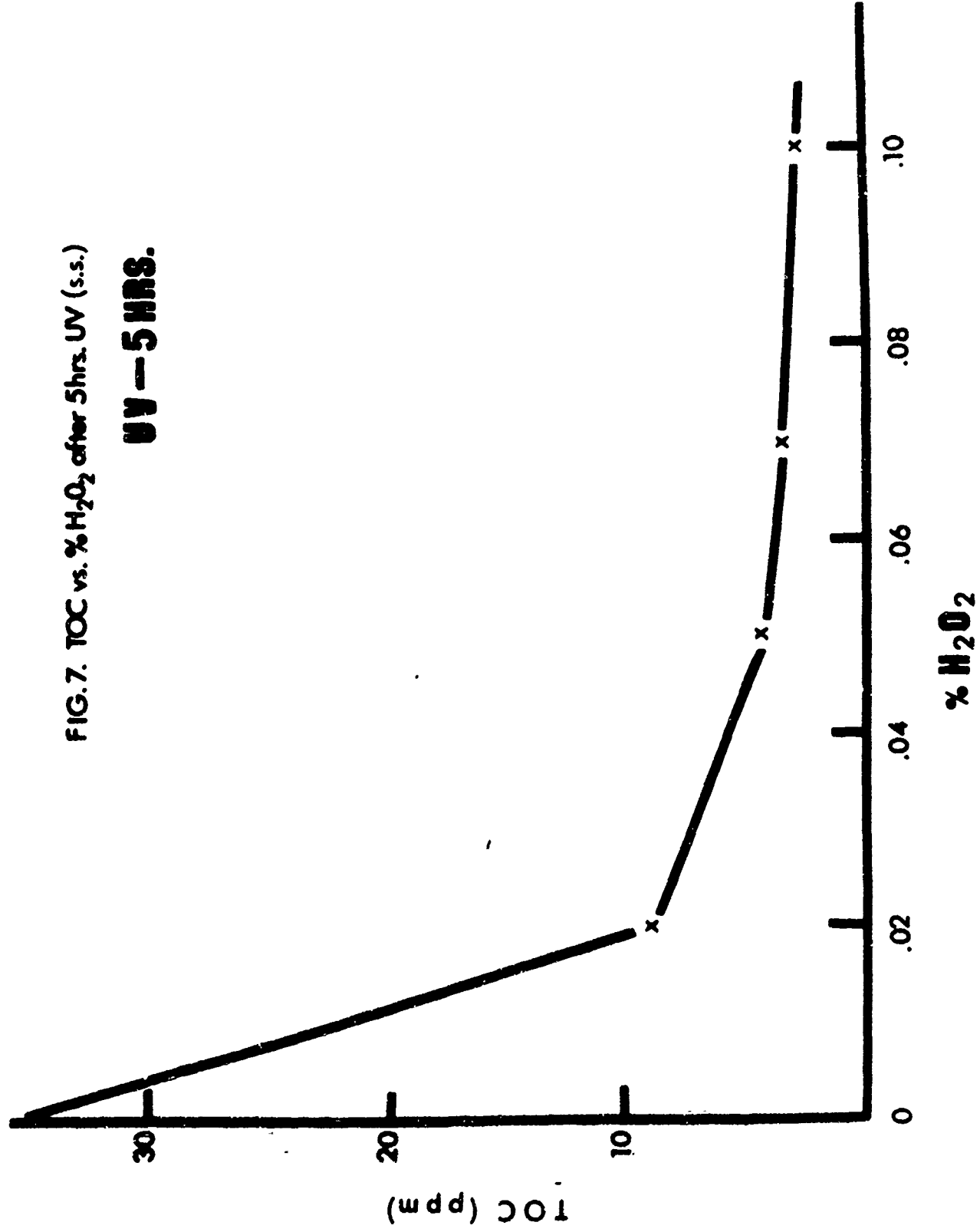
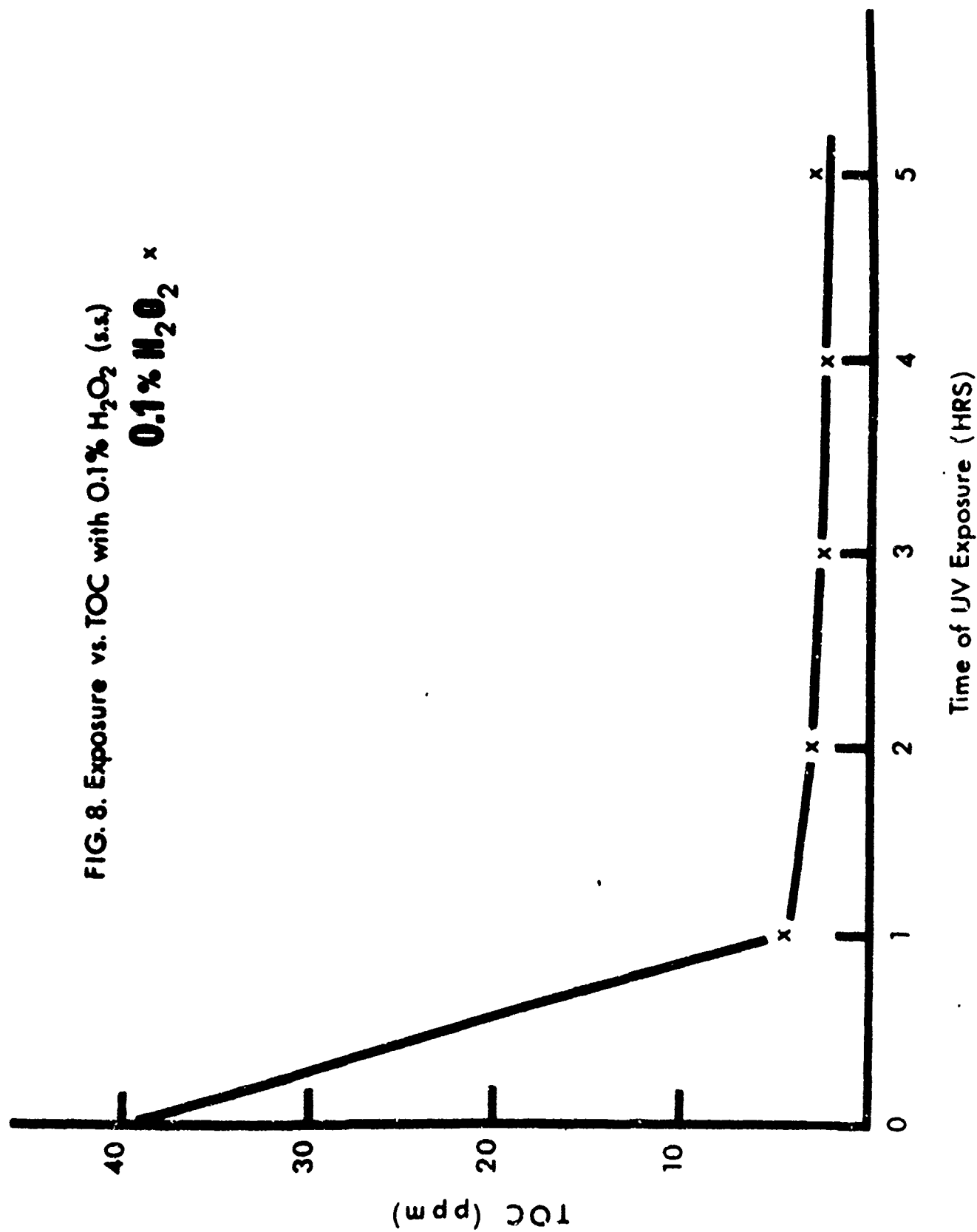


FIG. 8. Exposure vs. TOC with 0.1% H_2O_2 (s.s.)
0.1% H_2O_2 x



of all tested concentrations, was employed in this study. After 5 hours of irradiation recovery of $^{14}\text{CO}_2$ accounted for only 17% of the total expected activity. However, only one CO_2 trap was employed in the system and the system was not purged to force all the gases through the trap. About 13% of the activity was found in the photolysate. The remaining activity apparently was not trapped and had escaped in a gaseous phase. TLC studies had shown that no polynitroaromatics were detected in the photolysate which had a TOC concentration of about 3 ppm.

In another study (Study 2), employing multiple CO_2 traps (Fig. 4) and utilizing a purge system at the termination of the exposure period, it was discovered that the efficiency of our trapping system was increased dramatically. The new results indicated that 13.6% of the activity was recovered in the photolysate. This result is comparable with that of the first study in which 13% of the activity was discovered in the final photolysate. Two of the alkali traps accounted for 70.2% of the activity with no activity found in the third trap. This indicated that the $^{14}\text{CO}_2$ was not being flushed through the trapping system. Only 16.2% of the activity was unrecovered. Some of this activity could be attributed to the production of certain gases such as acetylene or methane which would not have been trapped.

This assay had shown that a very significant proportion of the TNT had been mineralized indicating that the TNT had actually undergone decomposition and not merely conversion in the system.

Gas Analysis: UV-H₂O₂ Static Treatment of a TNT Solution

A specific study was undertaken to indicate the types of gases produced from the UV-H₂O₂-static treatment of a saturated (100 ppm) TNT solution. A 0.3% H₂O₂ concentration was used (equivalent to three times the most effective concentration) to determine the extent to which the peroxide would be wasted. The gas production was measured in a water displacement apparatus and the gas analyzed by gas chromatography and infrared spectrophotometry to determine its composition. The individual concentrations of the gases were identified. The analyses have shown that oxygen comprised the greatest concentration (92%) of all the gases after the 2 hours of irradiation. CO₂ accounted for about 3% and nitrogen for 5.0%. No methane, nitrogen oxides, hydrogen or organic gases were detected. The temperature of the static system (48°C) obviously did not allow for any significant concentration of gases to be dissolved in the solution. Since the TNT solution could not have been boiled before treatment to drive out the dissolved gases, it is difficult to determine how much of these gases could be attributed to the gases originally dissolved in solution. However, it was determined that 200 ml of gas was collected from this treatment. A large percentage of the oxygen could more than likely be attributed to the decomposition of the H₂O₂ in the UV system, since such a great percentage could not have been present either in the atmosphere or in solution (~175 ml) initially. The production of oxygen is indicative of the great oxidative capacity of the H₂O₂ upon irradiation, and it illustrates that H₂O₂ is wasted if too much peroxide is employed for the task.

Cursory Examination of the Photolytic Products

The photolysates, after treatment in the static system, have been analyzed to identify the types of organics which are contributing to the residual TOC load. They have been examined for short chain carboxylic acids (2 to 5C in length) and formic acid by GC, and amino acids by TLC. Although no such short chain carboxylic acids have been detected, TLC studies have indicated the possible existence of amino acids in the photolysates. Further work is being undertaken to confirm this.

Since the detection of trinitrobenzene in the photolysates has illustrated that the TNT is demethylated early in the process, it is postulated that alcohols such as methanol and ethanol may be products of the treatment formed by the reaction of the methyl groups with the OH radicals and even with each other. Current studies are being undertaken to determine this.

UV-H₂O₂ Static Treatment of Explosives Other than TNT

Aqueous solutions of Explosive D (500 ppm), HMX (5 ppm), RDX (50 ppm), 2,4 DNT (100 ppm) and 2,6 DNT (100 ppm) were treated in the UV-H₂O₂ static system with excellent results. A summary of these results is illustrated in Table 12.

The results indicated that the UV-0.1% H₂O₂ static system worked efficiently and effectively in destroying Explosive D, HMX, RDX, 2,4 DNT and 2,6 DNT. TLC studies illustrated that all photolysates were void of these compounds and any detectable conversion products after only 1 hour of irradiation. Peroxide was being exhausted during the

TABLE 12. Summary of data from the UV-C.1% H₂O₂ static system treatment of aqueous solutions of Explosive D, HMX, RDX, 2,4 DNT and 2,6 DNT.

<u>COMPOUND</u>	<u>EXPOSURE (HR.)</u>	<u>ppm H₂O₂</u>	<u>TOC</u>
Explosive D	0	1000	168
"	1	~12	15.6
"	2	0	2.2
"	5	0	-
HMX	0	1000	-*
"	0.5	~100	-
"	1	>12 <50	-
"	5	0	-
RDX	0	1000	12.8
"	0.5	>5 <100	2.37
"	2.5	~3	-
"	3.0	0	-
2,4 DNT	0	1000	38.4
"	1	>12 <50	2.4
"	2	~1	-
"	5	0	-
2,6 DNT	0	1000	45.3
"	1	>12 <50	3.15
"	2	1	-
"	5	0	-

*Sensitivity of TOC analyzer insufficient to determine the concentration.

process. The TOC dropped very significantly in each case after 1 hour of irradiation.

After 2 hours of UV-H₂O₂ treatment of the Explosive D solution TOC load of the liquid was reduced by 98.7%. There was an 81% reduction of the TOC with RDX after 0.5 hour, 94% reduction of the TOC of 2,4 DNT solution and 93% of the 2,6 DNT TOC load after 1 hour of exposure. Within limits of detectability (1 ppm for Explosive D and 0.5 ppm for the other explosives), all these explosives appear to be eliminated by one hour of irradiation.

SUMMARY

Reviewing all the studies performed on the various UV systems, the UV-static-peroxide treatment appeared to yield the best results. Although not functioning under optimized conditions, the system successfully treated TNT, Explosive D, RDX, HMX, 2,4 DNT and 2,6 DNT contaminated solutions both efficiently and effectively. Each of these compounds was eliminated between 0 and 1 hour of exposure using 0.1% H₂O₂. A concurrent dramatic decrease in their TOC load was also observed. The organic material, consequently, was not merely being converted to related compounds, but was apparently being destroyed. The only conversion product noted in any of the photolysates after 1 hour of exposure was trinitrobenzene in the TNT irradiated solution. This product was found to be present in negligible amounts (10 to 50 ppb).

The UV-peroxide systems, in general, have provided us with workable decontamination procedures which result in the apparent degradation of

some very refractory molecules. In the case of TNT, both TOC and radio-tracer studies have illustrated that under given conditions over 90% of the original concentration of organic material was eliminated within one hour of exposure. No significant concentrations of toxic products have been found in any of the TNT solutions treated in the UV-0.1% H₂O₂ static system after 1 hour, or the UV-0.1% H₂O₂ continuous flow system after 7 hours.

Studies incorporating acetone in the UV continuous flow system were important because they prototyped the UV-peroxide system. However, the success of the UV-acetone treatment is questionable because of acetone's volatility and flammability, and because its contribution to the TOC concentration of the solution are undesirable qualities. The identity of the fluorescent product appearing in the UV-acetone TNT photolysates must also be resolved before the method can be considered effective. This will take time. It would therefore be more advantageous to place emphasis on a system which is already practical and workable such as the peroxide-UV system. However, the acetone-UV treatment should not and will not be ignored as a possible mode of treatment.

Since ¹⁴CO₂ has been shown to be a significant product in the degradation of ¹⁴C-TNT (1,3,5 labeled) in the 0.1% H₂O₂-UV-static system, it is not presumptuous to state that the TNT is actually being destroyed. It is, in effect, being mineralized to CO₂, which is the most desirable end-product of the TNT degradation process since it is completely innocuous. However, there is a residual TOC load (2-3 ppm) and some minor activity remaining in the photolysates after treatment which indicates this mineralization is incomplete. The product(s) remaining in the photolysate

must be identified and concentration(s) determined to be certain that the treated solution does not contain any toxic compounds. However, in all probability these compounds are likely to be short-chain aliphatics which are not very vulnerable to photochemical decomposition and which are environmentally safe and non-toxic to life.

Optimization of UV-H₂O₂ System

The UV-peroxide system has been shown to be relatively successful in treating explosive contaminated water. However, the UV system must be optimized to yield the most effective results in the shortest span of time. Optimum flow rate, maximum solution depth (distance from UV source), optimum UV energy, most effective peroxide concentration and its mode of administration, and optimum pH must be determined. The effectiveness of operating many UV treatment units in series or parallel to treat large volumes of contaminated water must be tested. This in turn would be dependent on all the aforementioned parameters.

It has been already established that the static system is more efficient than the continuous flow system. Consequently, in treatment of large volumes, the flow rate must be regulated to allow a sufficient constant exposure for the desired results. The maximum allowable distance from the UV source must also be established, since the solution's ability to utilize the UV energy as efficiently as possible is dependent on this factor. Colored solutions, because of their light and heat absorption properties will probably be more difficult to treat, dependent on the intensity of the color. The primary UV energy mode in which we are

currently operating is about 254 nm. Much energy is lost as heat. A different mode may be more efficient.

Throughout our studies peroxide was generally introduced to the explosive solution immediately before treatment. It is possible that small increments added on a continuous basis may result in greater efficiency with less waste of peroxide.

The pH of the solution generally drops significantly upon treatment. Control of the pH initially and/or throughout the treatment may be more advantageous than allowing the solutions to become acidic. Acidic solutions enhance the stability of the peroxide. This may be undesirable since the chief mechanism of the reaction is dependent on the decomposition of the peroxide to hydroxyl radicals which react with the organic material.

These are the chief parameters which must be established and controlled for the optimization of the UV treatment. This will be part of our main consideration in the development of a pilot system for large scale treatment of explosive contaminated solutions.

UV-Peroxide Treatment vs. Other Modes of Treatment

Many systems have been proposed for treating water solutions of explosives. Adsorption on charcoal or resin columns is effective but does not completely solve the problem. The explosive laden charcoal or resin must eventually be disposed or regenerated. Biological systems (5, 6) and chemical killing agents both generate by-products, which are perhaps more dangerous than the explosives. Incineration is impractical since usually less than 150 ppm explosive are normally soluble in water.

The UV-peroxide treatment has been shown in laboratory studies, under given conditions, to be very effective and to generate no detectable toxic compounds. The operational simplicity of the system and its low energy requirements combined with no specific need for skilled operating personnel should result in very low operating costs. If "off-the-shelf" engineering technology can be applied as expected, the capital costs should compare favorably with other systems. All in all, the potential and value of the UV-H₂O₂ treatment cannot be ignored by any environmentally conscious military centers active in the production, loading, and/or demilitarization of explosive materials. The process appears to be invaluable in its purpose in preventing the escape of harmful pollutants into the environment.

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APPENDIX A

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APPENDIX B

FOOTNOTES ON PROCEDURES

1. Method QTM-GC5, WQEC Chemical Standard Test Methods, Naval Weapons Support Center, Crane, Indiana.
2. Method QTM-TLC4, WQEC Chemical Standard Test Methods, Naval Weapons Support Center, Crane, Indiana. The method was modified to substitute Chandler's I solvent System for Hoffsommer's solvent, maintaining all other parameters but sample size which was reduced in most cases from 50 ml to 2 ml. The sample size analyzed was 2 ml unless otherwise stated.

Chandler's I Solvent System (4):

50 parts benzene
45 parts cyclohexane
5 parts ethyl acetate

3. Method QTM-LC2, WQEC Chemical Standard Test Methods, Naval Weapons Support Center, Crane, Indiana.
4. TLC method for analysis of RDX and HMX is found in Appendix C.
5. Cyanide: Specific ion electrode method; specific ion electrode Model 94-06, Orion Research Incorp., Cambridge, Massachusetts.
6. Nitrate: Method for Chemical Analysis of Water and Waste. U. S. E. P. A. 625-6-74-003, 1974, p. 197.
7. Nitrite: As above⁶, p. 215.
8. Ammonia: Specific ion electrode method; specific ion electrode model 8002-2. Electronic Instruments Ltd., England.
9. Analysis performed by GC-2A gas chromatograph equipped with thermal conductivity detectors. A more complete description of the procedure can be found in Appendix C.
10. Parameters for the determination of short chain organic acids can be found in Appendix C.
11. GC-mass spectrometry is run on a Hewlett Packard Model 5710A gas chromatograph interfaced to a Dupont Model 21-491 mass spectrometer.
12. IR spectra were run on a grating instrument, the Beckman IR20A infrared spectrophotometer.

APPENDIX C

DESCRIPTION OF METHODOLOGY AND ANALYTICAL PARAMETERS

ANALYSIS OF RDX AND HMX BY TLC

1.0 Water solutions of RDX and/or HMX are extracted with acetone. To make the acetone immiscible with water 23.3 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is added to each 50 ml sample in a separatory funnel, which is then shaken to dissolve the powder. An equal volume of acetone is then added to the sample and the sample again shaken. The layers are allowed to separate and the water layer is drawn off. The acetone layer is then poured into a beaker for evaporation. The acetone is evaporated to dryness and the dried sample is redissolved with 2 ml of acetone, transferred to a small test tube and evaporated again. To this concentrated sample is added 50 μl of acetone. A 20 μl sample is taken from the 50 μl and spotted on a silica gel thin-layer chromatographic plate. The silica gel contains a fluorescent indicator so that the separated material can be seen under a UV light (254 nm). (We have found that Kontes silica gel prescored plates, type LQDF, afford good reproducibility). Standards of RDX and HMX are also spotted and dried for development with the samples.

1.1 The spotted plate is then developed in a saturated TLC chamber containing petroleum ether (7 parts) and acetone (3 parts). After development of the solvent front (≈ 13 cm from origin) the plates are dried and viewed under a UV light (254 nm). The products appear as dark areas. The R_f values of HMX and RDX under these conditions are 0.30 and 0.43 respectively.

1.2 The sensitivity of this procedure is dependent on the detectability of the products by UV light. About $2 - 3 \times 10^{-7}$ g/spot is normally visible to the naked eye under UV light. This is the basic limitation of the procedure. For samples containing 5-10 ppb further concentration of the sample may be necessary.

1.3 It is important to note that all glassware used in the procedure should be acid-washed and/or disposable to prevent contaminants from appearing and interfering with the results.

GC GAS ANALYSIS PROCEDURE

Gas analysis of the resulting gases in UV degradation was accomplished using a Beckman GC-2A gas chromatograph equipped with thermal conductivity detectors.

A 1 cc gas sample was taken with a Pressure-Lok^R series A-2 1 cc gas syringe equipped with a miniature on-off valve for transporting the sample to the gas chromatograph.

The sample was injected onto a molecular sieve 5A gas chromatographic column. The column was a six foot long 1/4" O.D. stainless steel tubing.

The column was operated at 25°C and a helium flow of 40 cc/min thru the packing was maintained. The thermal conductivity detector was also at 25°C and was operated at 150 ma current and an attenuation of X1. A Hewlett Packard 1 mV strip chart recorder, Model 7127A, was used to record the chromatogram. This column and procedure separates hydrogen, oxygen-argon (occur together), nitrogen, methane, and carbon monoxide.

Second, an identical Beckman GC-2A gas chromatograph also equipped with thermal conductivity detectors was used fitted with a six foot 1/4" O.D. stainless steel column packed with Porapak Q; 80-100 mesh. This column operated at 25°C and 40 cc/min helium flow, will separate air, carbon dioxide, and nitrous oxide.

Detector parameters were the same as on the other gas chromatograph.

Electronic integration of the peak areas was done when possible using an Infotronic integrator, Model CRS-104.

PARAMETERS FOR THE DETERMINATION OF SHORT CHAIN ORGANIC ACIDS

GC: Hewlett Packard Model 3710A

Column packing: 60/80 mesh Carbopack B/3%
Carbowax 20m/0.5% H₃PO₄

Column dimensions: 30" x 1/4" O.D. 4mm I D. glass

Column temp.: 160°C

Detector temp.: 200°C

Injection port temp.: 200°C

Helium flow: 60 cc/min.

Sample size: 1 µl

Detector: FID 16x10⁻¹² AFS (amp full scale)

This packing allows analysis of underivatized free aliphatic acids in water down to 50 ppm in water. Includes formic acid as well as C₂-C₆ acids.

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